BUBBLE FORMATION AND GROWTH

Study of the Boundary Conditions at a Liquid-vapor Interface
through Irreversible Thermodynamics

by

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ABSTRACT

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The object of this theoretical investigation is to obtain a set of equations which will predict the behavior of a fluid as it changes phase across a plane surface. Irreversible thermodynamics is employed to obtain the general rate equations and the results of kinetic theory are used to determine the order of magnitude of several of the constants which appear in the rate equations. The present analysis is limited to phase change problems which are linear, that is the change in the driving potentials is small as compared to their value on either side of the liquid-vapor interface.

The equations which result from the analysis described above are applied to the condensation of a vapor on a plane liquid surface. From this example, the significance of the theory can be realized.

Author

LIST OF ILLUSTRATIONS

NOMENCLATURE

Symbol	Description
A	area
C_p	specific heat at constant pressure
E	energy
e	specific energy
H	enthalpy
h	specific enthalpy
h_{fg}	latent heat of condensation or evaporation
J_i	mass flux
J_u	energy flux
J_{qI}	heat transferred from reservoir
J_{qII}	heat transferred to reservoir
K	thermodynamic property defined by (36)
k	thermal conductivity
L_{uu}	defined as $(\partial J_u/\partial(d\tau))_{d\mu\tau=0}$
L_{ui}	defined as $(\partial J_u/\partial(d\mu\tau))_{d\tau=0}$
L_{ii}	defined as $(\partial J_i/\partial(d\mu\tau))_{d\tau=0}$
L_{iu}	defined as $(\partial J_i/\partial(d\tau))_{d\mu\tau=0}$
L_K	thermodynamic property defined by (17)
M	represents a non-equilibrium region
n	number of molds or mass units
P	pressure
Q	total heat transfer
$\bar{R}$	gas constant

NOMENCLATURE (Continued)

Symbol	Description
S	entropy
T	temperature
V	volume
v	specific volume
v_{fg}	difference in specific volume of vapor and liquid
v_x	velocity in x-direction
x	coordinate axes
α	represents a geometric surface
β	constant defined by (55)
λ	thermodynamic property defined by (16)
μ	chemical potential
ρ	mass density
σ	evaporation coefficient
τ	inverse temperature ($\tau \equiv 1/T$)

Subscripts

i	property at the interface
l	property of the liquid
M	property of the fluid in region M
m	momentum effect
R	property of the reservoir
s	saturation condition
v	property of the vapor
W	property at the wall
I	property of fluid in region I
II	property of fluid in region II
∞	property of fluid at infinity

I. INTRODUCTION

When a liquid and vapor coexist in equilibrium, the second law requires continuity of temperature and chemical potential across the liquid-vapor interface. However, if a finite rate of change of phase occurs, a discontinuity in temperature and chemical potential may exist at this interface. The magnitude of these discontinuities depend upon the rate at which the changes take place and the thermodynamic state of the system. Recently Sukhatme[1] presented experimental evidence that the discontinuity in temperature and chemical potential across the liquid-vapor interface had a significant effect on the heat transfer during film condensation of a liquid metal vapor. The effect of the discontinuities may also be important in other phase change processes and therefore it is important to obtain a theory which will predict the magnitude of the discontinuities and also to determine the effect they have on whatever process is occurring.

II. THE THERMODYNAMICS OF IRREVERSIBLE PROCESSES

The theory presented here is based on the principles of irreversible thermodynamics. Presently the theory of irreversible thermodynamics is applicable only to processes which are linear. Consequently the following analysis will be limited to these cases. For the present problem, a linear case is one in which the changes in temperature and chemical potential across the interface are small compared to the temperature and the chemical potential on either side of the interface.

The analysis will proceed according to the formalism of the following three steps. The explanations given for each step are essentially specializations of the more general explanations presented by Hatsopoulos and Keenan in reference (2).

1. The entropy production equation.

This equation expresses the rate of increase of entropy due to the irreversible phase change process. To express this in terms of other thermodynamic properties quasistatic regions are placed on each side of the liquid-vapor interface as shown in Figure 1. Region M represents the steady

but non-equilibrium region which exists between the homogeneous liquid
and vapor. The surfaces α' and α'' are placed such that the flow across
them is bulk flow. Regions I and II are maintained at a constant inverse
temperature γ and $\gamma + d\gamma$ by the reservoirs shown, and the pressure is
maintained constant throughout by the pistons.

The sole purpose of the entropy production equation is to determine
the appropriate forces and fluxes to be used in the phenomenological
equations. It will be shown later that for the present problem the forces
are $d\gamma$ and $d\mu\gamma$, and the fluxes are the rate at which mass (J_i) and
energy (J_u) are transferred across M.

2. The phenomenological equations.

For the present problem these consist of two equations which express
each flux as a function of both forces. The phenomenological equation for
the mass flux (J_1) is obtained as follows.

It is clear that (J_1) can be expressed as

$$J_i = J_i\left(\gamma, \mu\gamma, d\gamma, d\mu\gamma\right).\tag{1}$$

The function J_1 may be expanded into a Maclaurin power series as follows:

$$
\begin{aligned}
J_i(\gamma,\mu\gamma,d\gamma,d\mu\gamma) = &\ J_i\left(\gamma,\mu\gamma,0,0\right)\\
&+\frac{1}{1!}\left[\left(\frac{\partial J_i}{\partial(d\gamma)}\right)_{d\mu\gamma=0} d\gamma +\left(\frac{\partial J_i}{\partial(d\mu\gamma)}\right)_{d\gamma=0} d\mu\gamma\right]\\
&+\frac{1}{2!}\left[\left(\frac{\partial^2 J_i}{\partial(d\gamma)^2}\right)_{d\mu\gamma=0}(d\gamma)^2 +\left(\frac{\partial^2 J_i}{\partial(d\mu\gamma)^2}\right)_{d\gamma=0}(d\mu\gamma)^2\right]+\cdots
\end{aligned}\tag{2}
$$

When $d\gamma$ and $d\mu\gamma$ are zero, the system I-M-II is in an equilibrium state
and J_1 must vanish. The first term of the right-hand member of (2) must
therefore be zero. If we assume the derivitives which appear in (2) to
be fininte as $d\gamma$ and $d\mu\gamma$ go to zero, then it follows that

$$J_i = \left(\frac{\partial J_i}{\partial(d\gamma)}\right)_{d\mu\gamma=0} d\gamma + \left(\frac{\partial J_i}{\partial(d\mu\gamma)}\right)_{d\gamma=0} d\mu\gamma \tag{3}$$

as $d7$ and $d\mu7$ become small. By similar reasoning one can show that

$$J_u = \left(\frac{\partial J_u}{\partial (d7)}\right)_{d\mu7=0} d7 + \left(\frac{\partial J_u}{\partial (d\mu7)}\right)_{d7=0} d\mu7 \, . \tag{4}$$

For convenience Equations (3) and (4) are written in the following form;

$$\vec{J_u} = L_{uu}\, d\vec{7} - L_{ui}\, d\mu\vec{7} \tag{5}$$

$$J_i = L_{iu}\, d7 - L_{ii}\, d\mu7 \, , \tag{6}$$

where the definitions of the L's are obvious. The four L's are thermo-dynamic properties since the partial derivatives which define them are evaluated as the system approaches its equilibrium state. Equations (5) and (6) are known as the phenomenological equations.

The solution to the phase-change problem would be complete if the four L's in (5) and (6) were known. It will be shown in Section III that three of the L's can be expressed in terms of measurable quantities. The remaining one is obtained from the Onsager reciprocal relation.

3. **The Onsager reciprocal relation.**

For the present problem this relation becomes

$$L_{ui} = L_{iu} \tag{7}$$

III. **THE IRREVERSIBLE FLOW EQUATIONS**

To write the entropy production equation for the system shown in Figure 1, the pressure difference between regions I and II, due to momentum effects, will be neglected. In Section V it will be shown that this assumption is included in the assumption that the process is linear.

The total entropy production can be written as

$$\dot{S} = \dot{S}_I + \dot{S}_{II} + \dot{S}_M + \dot{S}_{RI} + \dot{S}_{RII} \, . \tag{8}$$

From the Gibbs equation it can be shown that

$$\dot{S}_I = \gamma \dot{E}_I + \gamma P \dot{V}_I - \mu\gamma \dot{n}_I ,$$

$$\dot{S}_{II} = (\gamma + d\gamma) \dot{E}_{II} + (\gamma + d\gamma) P \dot{V}_{II} - (\mu\gamma + d\mu\gamma) \dot{n}_{II} ,$$

$$\dot{S}_M = 0 \quad \text{(since the state in M is steady)}$$

$$\dot{S}_{RI} = -\gamma J_{qI}$$

and $\dot{S}_{RII} = (\gamma + d\gamma) J_{qII}$.

Substitution of these into Equation (8) yields

$$\dot{S} = \gamma \left(\dot{E}_I + \dot{E}_{II} - J_{qI} + J_{qII} + P\dot{V}_I + P\dot{V}_{II} \right) - \mu\gamma \left(\dot{n}_I + \dot{n}_{II} \right)$$
$$+ d\gamma \left(\dot{E}_{II} + P\dot{V}_{II} + J_{qII} \right) - d\mu\gamma \left(\dot{n}_{II} \right) . \tag{9}$$

Equation (9) can be simplified by applying the first law to system I-M-II. This gives

$$\dot{E}_I + \dot{E}_{II} = J_{qI} - J_{qII} - P\dot{V}_I - P\dot{V}_{II} . \tag{10}$$

Therefore Equation (9) becomes

$$\dot{S} = J_u \, d\gamma - J_i \, d\mu\gamma \tag{11}$$

where

$$J_u \equiv \dot{E}_{II} + P\dot{V}_{II} + J_{qII} = -\left(\dot{E}_I + P\dot{V}_I - J_{qI} \right) \tag{12}$$

and

$$J_i \equiv \dot{n}_I = -\dot{n}_{II} . \tag{13}$$

From Equation (11) it follows that the appropriate forces are $d7$ and $d\mu7$, and that the corresponding fluxes are J_u and J_1. Therefore the phenomenological equations become

$$J_u = L_{uu} \, d7 - L_{ui} \, d\mu7 \tag{14}$$

and

$$J_i = L_{iu} \, d7 - L_{ii} \, d\mu7 \tag{15}$$

Upon eliminating $d\mu7$ from (14) and (15) and introducing

$$\lambda \equiv \frac{L_{ui}}{L_{ii}} \tag{16}$$

and

$$L_k \equiv \left[L_{uu} - \frac{L_{ui} \, L_{iu}}{L_{ii}} \right] \tag{17}$$

the following result is obtained

$$J_u = \lambda \, J_i + L_k \, d7 \tag{18}$$

$$\frac{J_i}{L_{ii}} = \left(\frac{L_{iu}}{L_{ii}} \right) d7 - d\mu7 \quad . \tag{19}$$

Using the Onsager reciprocal relation it follows that

$$\lambda = \frac{L_{iu}}{L_{ii}} \tag{20}$$

and therefore

$$\frac{J_i}{L_{ii}} = \lambda \, d7 - d\mu7 \quad . \tag{21}$$

To express Equation (21) in terms of more familiar terms, it is necessary to find an expression for $d\mu7$. At equilibrium $(\mu7)_{sI}$ will equal $(\mu7)_{sII}$, therefore

$$d\mu7 = (\mu7)_{I} - (\mu7)_{II} = \left[(\mu7)_{I} - (\mu7)_{Is} \right] - \left[(\mu7)_{II} - (\mu7)_{IIs} \right] \tag{22}$$

where

$(\mu 7)_I$ is the actual $\mu 7$ in region I,

$(\mu 7)_{II}$ is the actual $\mu 7$ in region II,

$(\mu 7)_{IS}$ is the $\mu 7$ of region I, if it were at an

inverse temperature 7 and the saturation pressure

   P_s corresponding to 7 ,

$(\mu 7)_{IIS}$ is the $\mu 7$ of region II, if it were at an

inverse temperature 7 and pressure P_s .

However, the change in $\mu 7$ for a pure phase is $h_i \Delta 7 + v_i' 7 \Delta P$

Therefore

$$(\mu 7)_I - (\mu 7)_{IS} = v_I' \, 7 \, dP \tag{23}$$

and

$$(\mu 7)_{II} - (\mu 7)_{IIS} = h_{II} \, d7 + v_{II}' \, 7 \, dP \tag{24}$$

where

$$dP \equiv P - P_s . \tag{25}$$

It should be noted that dP is not an actual pressure drop which is realized in the system shown in Figure 1, but simply is the difference between the actual pressure (which is the same in I and II) and the saturation pressure P_s corresponding to the inverse temperature 7 (actual 7 in region I). By substituting (23) and (24) into (22) the following is obtained:

$$d\mu 7 = h_{II} \, d7 + 7 \left(v_{II}' - v_I' \right) dP . \tag{26}$$

Rewriting (18) for reference and substituting (26) into (21) gives

$$J_u = \lambda \bar{J}_i + L_k \, d7 \tag{27}$$

and

$$\frac{J_i}{L_{ii}} = \left(\lambda - h_{II} \right) d7 - 7 \left(v_{II}' - v_I' \right) dP . \tag{28}$$

For Equations (27) and (28) to be useful, λ must be expressed in terms of more easily measured properties. From Equation (27), one can write

$$\left(\frac{J_u}{J_i}\right)_{d\eta=0} = \lambda \tag{29}$$

Remembering the definition of J_u from Equation (12) the purpose for the following steps can be realized.

$$H_I = E_I + PV_I = e_I n_I + P \nu_I n_I$$
$$\dot{H}_I = \dot{E}_I + P\dot{V}_I \tag{30}$$
$$= e_I \dot{n}_I + P\nu_I \dot{n}_I$$
$$= -h_I J_i \tag{31}$$

Similarly

$$\dot{H}_{II} = \dot{E}_{II} + P\dot{V}_{II}$$
$$= h_{II} J_i . \tag{32}$$

Therefore Equation (12) can be written as

$$J_u = h_I J_i + J_{qI} \tag{33}$$

$$J_u = h_{II} J_i + J_{qII} \tag{34}$$

and it follows that

$$(h_{II} - h_I) J_i = J_{qI} - J_{qII} . \tag{35}$$

Now the object is to eliminate J_{qI} from Equation (33) or J_{qII} from Equation (34). However, to do this another relationship between J_{qI} and J_{qII} other than (35) is needed. For irreversible processes which do not involve a large finite change in any of the intensive thermodynamic properties, this relationship is obtained by defining a heat of transport, however, for the liquid-vapor system there is a large change in some of the intensive thermodynamic properties such as specific volume and specific energy, and therefore, the heat of transport in the usual sense is not a

useful definition. It will be shown that the following definition of K will yield the desired information.

$$K \equiv - \left(\frac{\bar{J}_{g\text{II}}}{J_{g\text{I}}} \right)_{d7=0} \tag{36}$$

It is important to note that K is defined only for an isothermal process.

By combining Equations (33), (35) and (36) one obtains

$$\left(\frac{J_u}{J_i} \right)_{d7=0} = h_\text{I} + \left(h_\text{II} - h_\text{I} \right) \frac{1}{1+k} \tag{37}$$

This shows that K is a thermodynamic property, since $\left(J_u / J_i \right)_{d7=0}$ is a thermodynamic property.(See Equations (29) and (20).

With the use of Equations (37) and (29), Equations (27) and (28) become

$$J_u = \frac{1}{k+1} \left[k h_\text{I} + h_\text{II} \right] J_i + L_k \, d7 \tag{38}$$

$$\frac{J_i}{L_{ii}} = \frac{k}{k+1} \left[h_\text{I} - h_\text{II} \right] d7 - 7 \left(v_\text{II} - v_\text{I} \right) dP \,. \tag{39}$$

Note that in (38) and (39) there are three unknown thermodynamic prep-erties K, L_{11} and L_K. The following three equations, which are obtained from (38) and (39), indicate the experiments which could be performed to measure these constants.

$$\left(\frac{dP}{d7} \right)_{J_i = 0} = \left(\frac{k}{k+1} \right) \frac{h_\text{I} - h_\text{II}}{7 \left(v_\text{II} - v_\text{I} \right)} \tag{40}$$

$$\left(J_i \right)_{d7=0} = -L_{ii} \, 7 \left(v_\text{II} - v_\text{I} \right) dP \tag{41}$$

$$\left(J_u \right)_{J_i = 0} = L_K \, d7 \tag{42}$$

IV. MEANS OF OBTAINING K AND L₁₁ FROM KINETIC THEORY

To obtain the order of magnitude of K and L_{11} the results of a kinetic theory analysis performed by Schrage[3] will be used. These are

$$\left(\frac{dP}{dT}\right)_{J_i=0} = -\frac{1}{2}\frac{P}{T} \tag{43}$$

and

$$\left(J_i\right)_{dT=0} = \sigma\left(\frac{T}{2\pi \bar{R}}\right)^{1/2} dP \tag{44}$$

With (43), (44), (40), and (41) one obtains

$$\frac{k}{k+1} = \frac{P}{2}\frac{v_{fg}}{h_{fg}} \tag{45}$$

and

$$L_{ii} = -\frac{\sigma}{(2\pi T\bar{R})^{1/2} v_{fg}} \tag{46}$$

Substitution of (45) and (46) into (38) and (39) yields

$$J_i = \frac{\sigma P T^{1/2}}{(2\pi\bar{R})^{1/2}}\left[\frac{1}{2}\frac{dT}{T} + \frac{dP}{P}\right] \tag{47}$$

and

$$J_u = \frac{1}{k+1}\left[kh_I + h_{II}\right]J_i + L_k dT. \tag{48}$$

V. JUSTIFICATION FOR NEGLECTING THE MOMENTUM PRESSURE DROP

If the momentum effect is included, Equation (26) becomes

$$dJT = h_{II} dT + T(v_{II} - v_I)dP + Tv_{II} dP_m \tag{49}$$

where dP_m is the momentum pressure difference across M. From the momentum and continuity equations it is easy to show that

$$dP_m = -J_i^2(v_{II} - v_I). \tag{50}$$

Therefore Equation (49) becomes

$$dJT = h_{II} dT + T(v_{II} - v_I)(dP - v_{II} J_i^2). \tag{51}$$

To obtain the order of magnitude of $v_{II} J_i^2$ Equation (47) is used

$$dM = h_{II} d\tau + \tau (v_{II} - v_I) \left[dP - v_{II} \frac{v^2 P^2 \tau}{2 \pi R} \left(\frac{1}{2} \frac{d\tau}{\tau} + \frac{dP}{P} \right)^2 \right] \tag{52}$$

Equation (52) is substituted into Equation (21) where λ is obtained from (38) and (45). After several algebraic steps this yields

$$\frac{J_i}{(v_{II} - v_I) P \tau L_{ii}} = - \frac{1}{2} \frac{d\tau}{\tau} - \frac{dP}{P}$$
$$+ \frac{v_{II} v^2 P \tau}{2 \pi R} \left[\frac{1}{4} \left(\frac{d\tau}{\tau} \right)^2 + \frac{d\tau dP}{\gamma P} + \left(\frac{dP}{P} \right)^2 \right] \tag{53}$$

where the momentum effect is contained in the last three terms in Equation (53). The use of the Onsager relation presupposed that therms of the order of $(dP/P)^2$ and $(d\tau/\tau)^2$ were negligible compared to dP/P and $d\tau/\tau$, therefore, the momentum effect will also be negligible since they are of the order of $(dP/P)^2$ and $(d\tau/\tau)^2$.

VI. APPLICATION OF THE IRREVERSIBLE FLOW EQUATIONS TO CONDENSATION AT A FLAT SURFACE

Figure 2 shows a vapor condensing at a plane liquid surface. The purpose of this analysis is to determine the temperature of the vapor at the liquid-vapor interface (T_{vi}). Since the expression for J_u was not known, previous investigators have assumed the temperature of the vapor to be a constant, however, it will be shown that this assumption may be in error.

If the vapor is assumed to be a perfect gas and if viscous heating is neglected, the energy equation becomes

$$\frac{\partial T}{\partial x} = - \beta \frac{\partial^2 T}{\partial x^2} \tag{54}$$

where

$$\beta = - K_v / (\rho_v C_p v_x) \tag{55}$$

Note that β is a constant positive number, since $\rho_v v_x$ is a positive constant from the continuity equation. Integration of Equation (54) with

the following boundary conditions

$$T(\infty) = T_\infty \tag{56}$$

$$T(0) = T_{vi} \tag{57}$$

yields

$$T - T_\infty = (T_\infty - T_{vi}) \, e^{-\frac{x}{\beta}}, \tag{58}$$

and it follows that

$$\left(\frac{dT}{dx}\right)_{x=0} = \frac{1}{\beta} (T_\infty - T_{vi}) . \tag{59}$$

To determine $(dT/dX)_{X=0}$ it is necessary to consider the heat transfer at the liquid-vapor interface. Since there is bulk flow in the vapor near the interface one can write

$$J_u = h_v J_i + \left(\frac{Q}{A}\right)_v \tag{60}$$

where $(Q/A)_v$ is the heat transferred in the positive X direction. Equating this expression for J_u to the one given by Equation (38) it follows that

$$\left(\frac{Q}{A}\right)_v = \left(\frac{-k}{k+1}\right) h_{fg} \rho_v \, v_x + L_k \, dT . \tag{61}$$

Substituting for K/K+1 from Equation (45) yields

$$\left(\frac{Q}{A}\right)_v = - \frac{P}{2} \, v_{fg} \rho_v \, v_x + L_k \, dT . \tag{62}$$

Combining (62) with (59) it follows that

$$(T_{vi} - T_\infty) = \frac{P v_{fg}}{2 C_p} + \frac{\beta L k}{k_v} \, dT . \tag{63}$$

Note that if $L_K = 0$ and $v_{fg} = v_v$ Equation (63) becomes

$$\frac{T_{vi} - T_\infty}{T_{vi}} = \frac{1}{2} \frac{\bar{R}}{C_p} \tag{64}$$

This shows that the interface temperature may be quite different from T_∞.

VII. CONCLUSIONS AND RECOMMENDATIONS

From the above results it is concluded that the problem of a phase change can be successfully analyzed from the point of view of irreversible thermodynamics.

An expression for the energy flux (J_u) across the liquid vapor interface was obtained. No such expression could be found in the literature surveyed. This expression is important because it permits one to determine the temperature at the interface.

The present analysis is limited to steady interphase transfer across a plane surface, however, it is felt that the analysis may be extended to include the unsteady interphase transfer across a curved surface.

The linear approximation made in this analysis greatly restricts its applicability. For this reason the extremely complex non-linear problem should be investigated.

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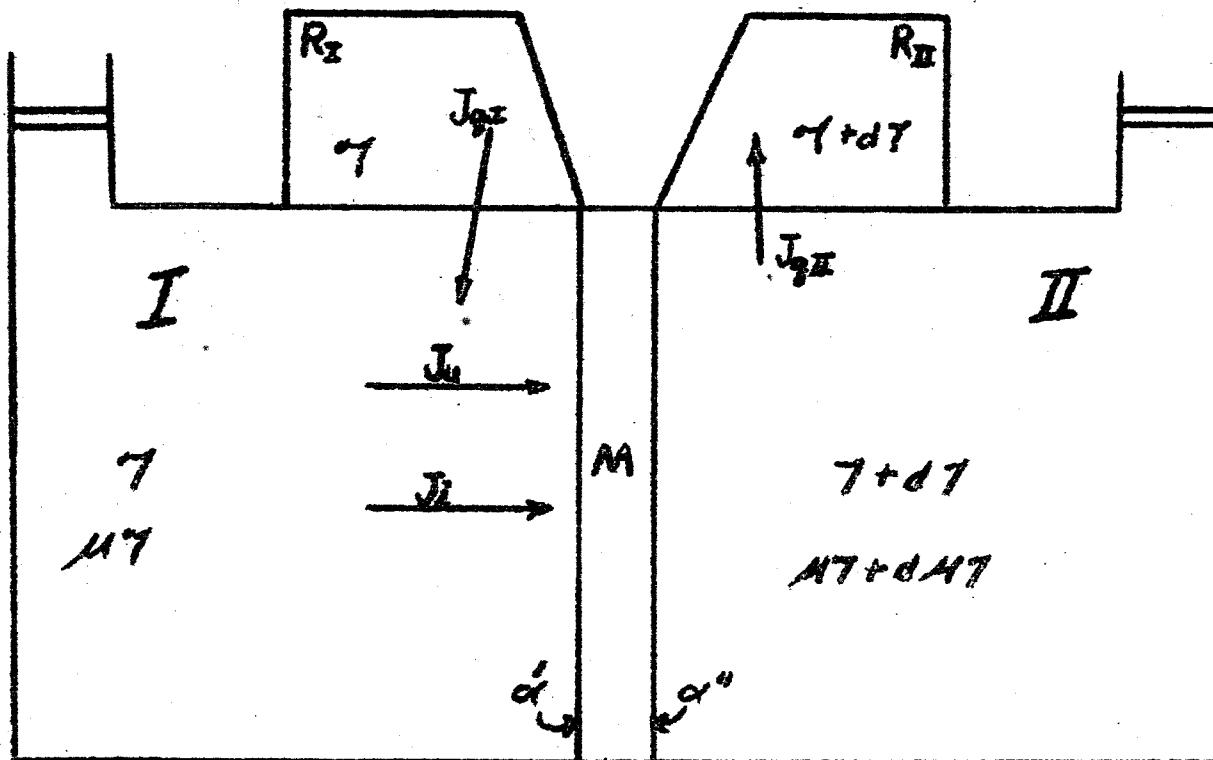
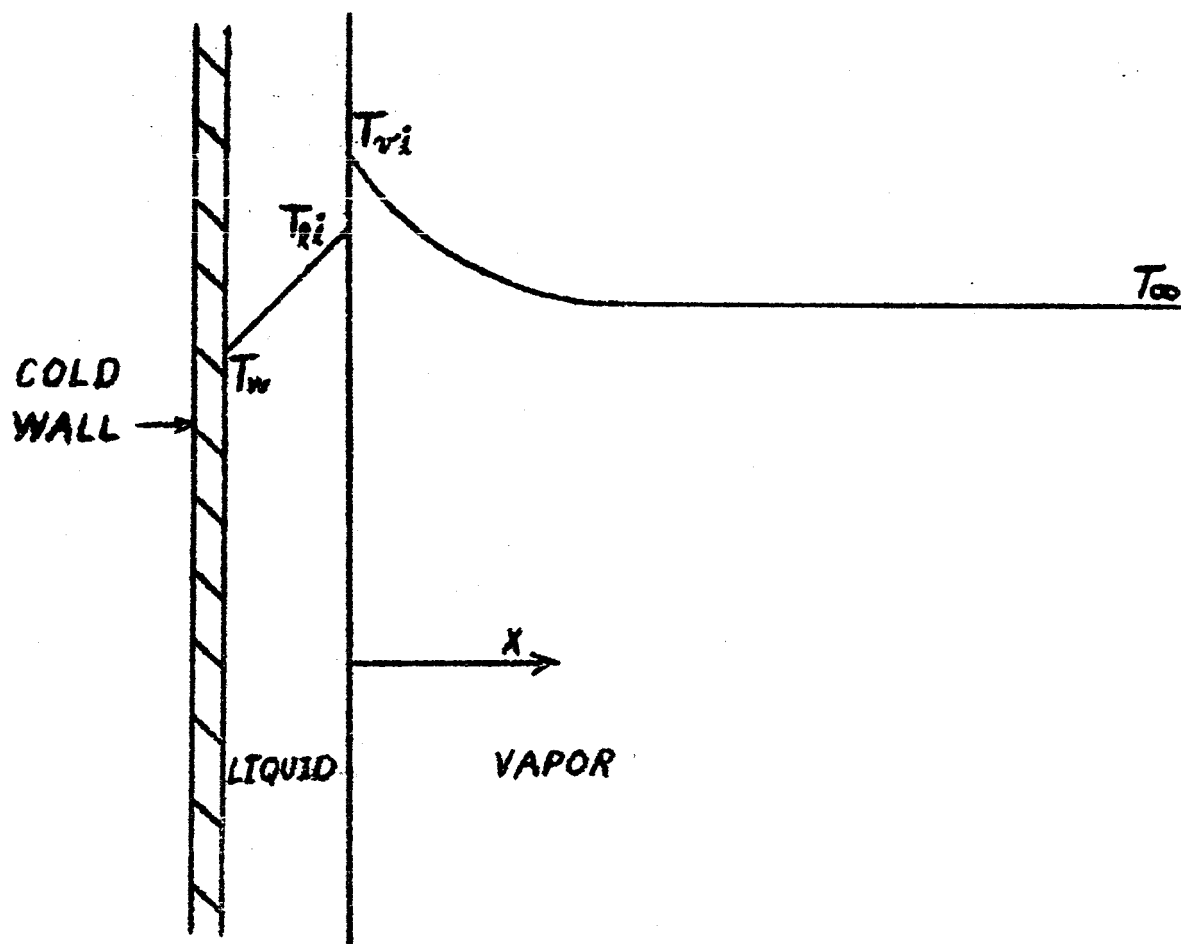FIGURE 1. SCHEMATIC OF MODEL USED TO CALCULATE THE ENTROPY PRODUCTION

FIGURE 2. THE CONDENSATION OF A VAPOR AT A PLANE SURFACE